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Gaseous Emissions from Excess Air Combustion of Explosives and Propellants

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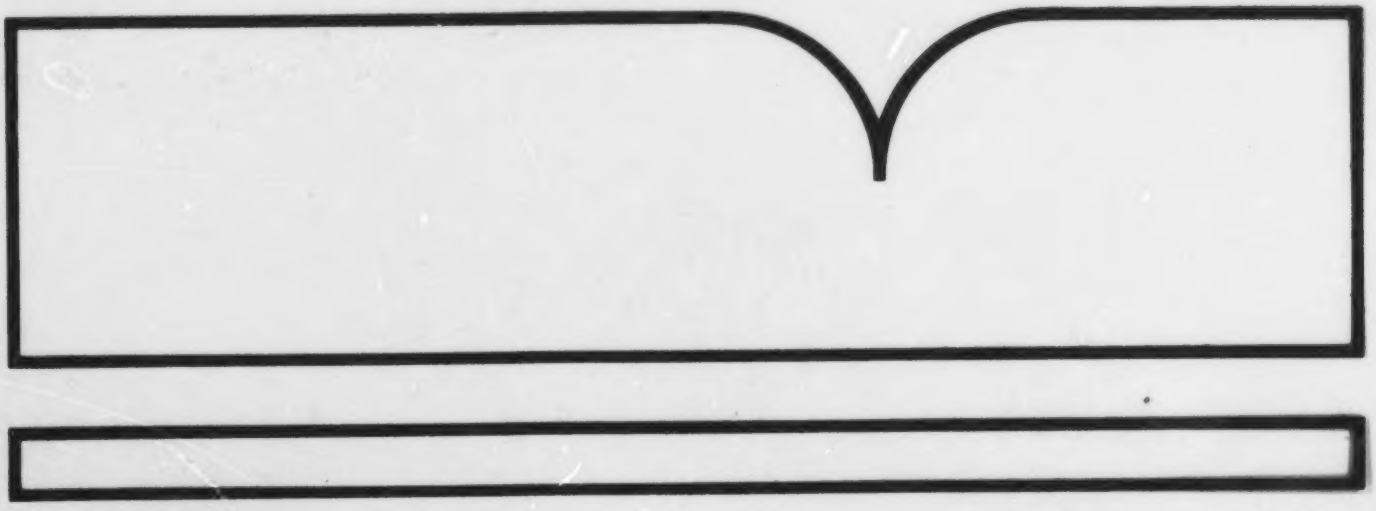

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GASEOUS EMISSIONS FROM EXCESS AIR COMBUSTION OF EXPLOSIVES AND PROPELLANTS

by

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16. ABSTRACT

The purpose of this short-term project was to determine the levels of nitric oxide (NO), nitrogen dioxide (NO_2), and carbon monoxide (CO) in the off-gases from the open burning of explosives in excess air. The ultimate goal is to reduce the level of NO_x, CO, and particulates emitted during the destruction of surplus, waste, and off-spec, explosives. Previous work (DOE) showed that a gravel/sand filter in the roof of a bunker reduced the level of particulates emitted during excess air combustion of propellants (only limited NO_x or CO measurements were reported). In this project, two HMX-($C_4H_8O_8N_8$)-based propellants (Chaparrel, 200 to 538 g, and Arcadene 313B, 65 to 162 g) were burned in a 1.3 m^3-steel chamber fitted with a 30-cm-deep sand and gravel filter. Air (1 to 6 m^3/min) was blown into the chamber to ensure combustion and to force the gases through the filter, which included a 2-cm layer of damp activated carbon. The NO-concentration was the predominant and most reproducible for the components measured. Little NO_2 was observed. CO-production fluctuated widely, probably due to inadequate mixing of the gases within the chamber and uneven burning. The NO and CO concentrations decreased across the filter. NO-reductions were 25 to 67% for Arcadene and 10 to 57% for Chaparral; CO-reductions were from 38 to 81% for Arcadene and 33 to 91% for Chaparral. The project demonstrated that the filter is effective in partially eliminating NO and CO emissions, but that additional work, including the incorporation of catalysts in the bed and the introduction of NO-control gases (e.g., NH_3), should be undertaken.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

The safe disposal of high energy materials (explosives, propellants) is an ongoing problem for both military and commercial manufacturers and users. That such disposal practices are environmentally acceptable and have minimal impact present additional constraints requiring the application of unusual and innovative approaches. This project was an effort to develop and evaluate one such approach for this difficult area.

Francis T. Mayo
Director
Municipal Environmental Research
Laboratory

ABSTRACT

The purpose of this short-term project was to determine the levels of nitric oxide (NO), nitrogen dioxide (NO_2), and carbon monoxide (CO) in the off-gases from the open burning of high explosives in excess air. The ultimate goal is to develop and demonstrate an improved technique for open air burning of surplus, waste, over-age, and out-of-specification high explosives (including propellants) so that the level of released particulates and noxious gases is much reduced from the level that is common when the explosive is destroyed by detonation or conventional open air burning. Data are available on the composition of gases and vapors released from explosives in actual use situations (blasting, rocket propulsion) in which all (or most) of the oxygen is provided by the explosive itself; but there are little data available on the combustion products formed during burning (or incineration) in excess air. Previous work (DOE) showed that a gravel and sand filter installed in the roof of a bunker significantly reduced the level of particulates emitted during the excess air combustion of high explosives but few NO_x or CO measurements were reported.

In the project herein reported, two HMX-($C_4H_8O_8N_8$)-based propellants, Chaparral 6678 (200 to 538 g) and Arcadene 313B (65 to 162 g), were burned in a specially built, 1.3 m^3-steel chamber fitted with internal baffles and a top-side 30-cm (12-in.)-deep, layered, sand-on-gravel bed (ca. 0.8 m^2 (1 yd^2) in area) also containing a 2.5-cm (1-in.)-layer of damp granulated activated carbon. A blower furnished 1 to 6 m^3/min (35 to 210 acfm) of air to the chamber to ensure smooth combustion and to force the off-gases, vapors, and particulates through the filter bed. Thermocouples and gas analysis probes were installed above and below the filter to monitor gas/vapor temperatures and compositions.

More than 50 burns were conducted merely to determine the optimum quantities of explosive, air flowrates, position of baffles, and location of the sensors. Nonetheless, the results of the 15 tests-of-record were quite variable. The NO concentration was both the most prominent and reproducible for the components sampled. Little NO_2 was observed. CO production fluctuated widely for reasons that are incompletely understood but that may relate to inadequate mixing of the gases, fluctuating contact between air and uneven burning of the propellant. NO reductions across the filter were 25 to 70% for Arcadene and 10 to 57% for Chapparal; CO reductions were 38 to 81% for Arcadene and 33 to 91% for Chaparral.

Note that, when HMX explodes in the absence of air, one mole (MW = 296) should stoichiometrically yield 4 moles each of N_2, CO, and H_2O, which is equivalent to 270 L (@STP) and, assuming the water exists as steam, corresponds to 330,000 ppm of CO. For the samples tested, assuming burn

times of 1 min @ 2.4 m^3/min of added air, the average CO level should be about 40,000 ppm, assuming no conversion to CO_2. In this work, time-averaged, maximum concentrations for CO are less than 400 ppm, which indicates considerable conversion of CO to CO_2. On the other hand, the quantity of NO_x produced may be higher in open air burning than during explosions.

The project demonstrated that the filter used is effective in partially eliminating NO and CO emissions and verified that particulates are trapped by the filter. Additional work--including the incorporation of catalysts in the bed and the addition of NO-control gases (e.g., NH_3)--should be undertaken.

This report was submitted in fulfillment of Job Order R-52 (IT Purchase Order No. E10-81-1) of EPA Contract 68-03-3069 with IT Corporation. Atlantic Research Corporation was awarded a subcontract to perform the experimental work and produce a report on the data. The report covers the period from October, 1981 to December, 1981 (experimental work); work was completed as of June, 1982.

CONTENTS

Foreword..... iii
Abstract..... iv
Figures..... vii
Tables..... vii
Acknowledgement..... viii

1. Introduction..... 1
2. Conclusions and Recommendations..... 5
3. System Preparation..... 7
   Equipment..... 7
   Explosives and Gases..... 11
   Procedures..... 11
4. Experimental Procedures..... 13
   Preliminary Test Burns..... 15
5. Results and Discussion..... 16

References..... 21

FIGURES

Number		Page
1	Schematic of combustion chamber	8
2	Combustion chamber	9
3	Experimental set-up	10
4	Slab of Chaparral propellant prepared for ignition	14

TABLES

Number		Page
1	Approximate Composition of Chaparral Propellant	12
2	Arcadene 311B (C-4) Composition	12
3	Combustion of Chaparral 6678 and Arcadene 311B	17
4	Combustion of Chaparral	18
5	Combustion of Arcadene 311B (C-4)	18
6	Yield of Gaseous Products from the Isothermal Degradation of HMX	19
7	Composition of PBX 9404	20
8	Selected Data from High Explosive Incineration	20

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SECTION 1

INTRODUCTION

The proper handling of explosives and propellants[1,2,3], for both military and commercial uses, requires--among other considerations--that excess materials, products outside of specifications, and out-of-date materials be disposed of safely. Often the very properties that make such waste materials unsuitable for use also increase the risks inherent in their disposal. The sensitivity and high energy of explosive materials impose unique constraints and limitations on suitable and cost-effective, particulate and noxious gas emission-control equipment that may be used in conjunction with available disposal systems.

Among the conventional methods of disposal for high explosives detonation, open burning, and incineration in a variety of specially designed chambers are the most widely used procedures. Traditionally, excluding incineration, these processes have been carried out in remote areas without any control of the gaseous or particulate emissions generated by the destruction. Recently, however, there has been interest in assuring that such operations do not contribute to air or water pollution.

At this time, detonation and open burning are the preferred methods, of disposal since these require minimum handling of sensitive materials and allow the materials to be destroyed with the least likelihood of creating an unsafe situation, as might occur in a confining chamber i.e., incinerator. Both procedures are convenient, very economical, and relatively safe. Although the processes are, wherever possible, carried out in remote locations, detonation can result in excessive noise and disturbing shocks, and both processes produce uncontrolled emissions of particulate matter and noxious gases such as NO, NO_2, CO, N_2O, and even HCN. The technology is such that control of emissions cannot be accomplished readily. Where large quantities of explosives and propellants must be disposed of, such emissions may be a nuisance, exceed allowable emissions, or contribute to excessive ambient air levels of the pollutants and possibly to acid rain formation.

Incineration, which involves the controlled thermal oxidation of sensitive materials in a chamber, allows more precise control of the process and emissions. However, this processing route is more expensive in both capital and operating costs, partially because of the special handling requirements and partially because of the control equipment needed to minimize emission of combustion products.

Low cost control of emissions from incineration and other combustion processes (excluding detonation) would make such alternatives more attractive to industry and public groups. This study evaluated one such

method[4], which was originally examined as a means of controlling particulate emissions, for also reducing gaseous emissions of NO, NO_2, and CO from the combustion of explosives. Fundamental studies have demonstrated that N_2, H_2O, and CO are the major gaseous combustion products from the actual use of high explosives and propellants, while NO, N_2O, NO_2, CO_2, and HCN are other possible products. Depending on the formulation of the explosive, particulates can be released in significant quantities. The effectiveness of the system used in this project is based on the reduction in concentration of particulates, NO, and CO when the combustion occurs with excess air and the combustion products then pass through a sand/gravel filter bed.

In general, explosive (and pyrotechnic) materials consist of solid or liquid compounds or mixtures that, when shocked or ignited, quite rapidly release heat and convert almost completely to hot gases, vapors, and particulates with no requirement for oxygen other than what is self-contained. Typical detonators (initiating explosives) include lead azide ($Pb(N_3)_2$) and PETN ($C_5H_8N_4O_{12}$), which create shocks to set off high explosives such as RDX ($C_3H_6N_6O_6$) or dynamite ($C_3H_5N_3O_9$ with 24.5% diatomaceous earth and 0.5% sodium carbonate). A good example of a low explosive is black powder (74% KNO_3, 15.6% charcoal, 10.4% S). High explosives include many formulated blasting agents (ammonium nitrate (94%) + fuel oil (6%)) and propellants (HMX compositions) used industrially or in munitions or rocketry, where extreme brisance (shattering) is not needed or required. (Grenades, shells, bombs, and remotely guided missile warheads require high explosives designed for metal shattering; the propellant that drives a round from a cannon does not.) The major products generated by typical explosives are nitrogen, steam, and carbon monoxide, as well as particulates from incomplete combustion or, more generally, from the special additives in formulated explosives.

In low explosives, the sound accompanying the release of energy resembles a "whoosh", initiation is usually by ignition, time of conversion to gaseous products is measured in milliseconds, velocity of combustion is ca. 5 to 7.5 cm/sec (2 to 3 in./sec), flame-front velocity is 500 to 1600 m/sec (1/3 to 1 mile/sec), and pressure of the explosion is up to 3.4×10^4 kN/m^2 (50,000 psi). For detonators or high explosives, the sound resmbles a boom or clap, initiation is by shock (as from a detonator) heat, or a spark, conversion time is measured in microseconds, velocity of consumption of 1600 to 10000 m/sec (1 to 6 miles/sec), velocity of the flame front is similar, and pressure ranges from 3.4×10^4 to 2.7×10^7 kN/m^2 (50,000 to 40,000,000 psi). All explosives produce overpressures in the atmosphere and the detonators generate shock waves.

Explosives generally fill their containers more or less completely so that, when the explosion occurs, the great energy release (heat) and change in PV (pressure x volume product) produce hot, high pressure gases from the solid explosive; extreme, disintegrative or propulsive forces are unleashed. For propellants (especially for rocketry), controlled burning is required so that steady, predictable thrust can be generated (the newly released gases and particulates react against what has already been released (Newton's 3rd law); solids, including metal powders, are added for a variety of reasons).

Consider RDX (Cyclonite, $C_3H_6N_6O_6$, hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX ($C_4H_8O_8N_8$, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine). Assuming the nitrogen forms N_2 gas and the hydrogen forms H_2O (steam), there is just enough oxygen remaining to form CO. When one considers kinetics, equilibria, and side reactions, it is not surprising that N_2O, NO, NO_2, C (soot), HCN, as well as some free radicals are also formed: N, H, and O atoms and OH radicals.

On the other hand, nitroglycerine ($C_3H_5N_3O_9$) stoichiometrically should form 1.5 N_2, 2.5 H_2O, and 3 CO_2 with one 0.5 O left over (perhaps to form 0.5 N_2O). (Note absence of CO.) For most high explosives, however, CO is a major product, which is advantageous since less (bound) oxygen is required than to form CO_2 and either gas will occupy the same volume, with CO behaving more ideally as a gas and thus exerting more pressure.

Black powder (gunpowder), a low explosive, is generally formulated to form K_2S, N_2, CO_2, and CO, but SO_2, K_2SO_4, K_2S, and other compounds have also been identified.

In passing, one should note the existence of hypergolic materials, which are separated materials that react vigorously on mixing (the rocket fuel composed of nitrogen tetroxide (N_2O_4) and a mixture of hydrazine (N_2H_4) and substituted hydrazines [$(CH_3)_2N\text{-}NH_2$] is an example). A variety of combinations of hydrogen, oxygen, fluorine, boron, and peroxides form hypergolics that are commonly used in rocketry--no further consideration is given to hypergolics herein.

To return to the high explosives and propellants that are formulated from HMX, RDX, Dynamite, nitrocellulose, etc., the disposal problem being addressed is twofold: (1) to reduce or eliminate the nitrogen oxides and CO released during destruction and (2) to remove the particulates that may form intentionally (as part of the formulation) or from kinetic/thermodynamic considerations. Water, CO, and N_2 are odorless, and CO_2 is almost so, so that the odor associated with the use or destruction of explosives comes from other gases such as NO, NO_2, NO_x, sulfur oxides, etc. In the case of ANFO (ammonium nitrate and fuel oil) explosives or of ammonium perchlorate, the gaseous products may be especially irritating to humans and may contribute to formation of photochemical smog.

One should not be left with the impression that burning of explosives without application of air pollution control systems is the universal practice. Rounds and detonators (including components of mines and shells) are often incinerated at a safe feed rate in thick wall furnaces to collect the metal (brass, lead, steel) for recovery. Detonators are frequently disposed of by dropping them (also at a controlled rate) into heated pans in an incinerator. The off-gases and particulates usually pass through cyclones and bag houses. The most commonly regulated emissions are particulates and NO_x.(3)

A major advance was the work by DOE (4) that showed quantities of certain propellants could be burned with excess air in bunkers equipped with gravel/sand tops for removal of the major fraction of particulates. Under

the proper design conditions, existing particulate emission regulations could readily be met.

With this work as a starting point, the intent of this project was to find a way of conducting open burning so that the level of NO_x, CO, and even SO_x could also be lowered to levels that are more commonly accepted, such as those from power plants or automobiles.

By their very design, some high explosives produce CO in quantity; CO is not readily converted to CO_2 unless excess oxygen and possibly catalysts are present. (Note that at thermodynamic equilibrium, C, CO, and CO_2 must co-exist.) The problem with NO is perhaps more difficult since the conversion of NO to NO_2 is slow and, further, high temperatures favor the formation of nitrogen oxides from the nitrogen gas that is almost always a principal product of the decomposition of explosives (in actual use or during disposal). The nitrogen/oxygen reaction is complex; but, one can generally expect NO_x to become a problem at temperatures of 1200-1500 ^{o}C. Unfortunately, there are many temperatures to be considered (flame, gas, wall, product) and the formation and dissociation of NO_x is condition-dependent.

In this project, the goal was to obtain some baseline data on what levels of CO and NO_x one might expect during open burning of explosives in excess air. A next phase would consider improved ameliorative measures (only a thin layer of granular activated charcoal (GAC) was used in this work and GAC is not a really good adsorber for CO and NO).

The work was conducted at a very low level of funding; the results, though not of the highest quality, do indicate that there are significant differences in the products of the decomposition of explosives in actual use (or in the in-field detonation of surplus material) and in controlled, excess air burning. The work was not performed in an incinerator, as that term is commonly understood. The quantity of material burned was selected so that no explosion (but, rather, free burning) took place. The ultimate goal is to determine what simple, cheap, air pollution systems can be used to reduce the level of undesirable emissions.

Note should be taken that it is not always practical or expedient to make any attempt whatsoever to protect the environment when explosives must be disposed of. Bomb squads are no more subject to arrest for violation of air pollution regulations than are owners or tenants whose buildings burn, each group having in common the "permission" to allow air to become "dirty"--albeit for different reasons.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results of tests on the excess air combustion of high explosives in a steel chamber fitted with a charcoal-containing sand and gravel filter (1) indicate that the levels of the evolved nitric oxide (NO) and carbon monoxide (CO) are effectively lowered, and (2) verify a prior observation that particulates are efficiently removed.

By the reaction of CO with O_2 in the air, the level (quantity) of CO is much reduced over what is common during confined combustion (propellants) or during explosions. The filter is effective in further reducing the level of noxious gas (CO, NO, etc.) concentration during passage through the composite bed.

Definitive values for the achievable reduction of each gas level cannot be presented because of the wide variation in data. Specifically, NO reductions by the filter ranged from 25 to 67% for Arcadene 311B and 10 to 57% for Chaparral; CO reductions ranged from 38 to 81% for Arcadene 311B and from 33 to 91% for Chaparral. (Arcadene and Chaparral are HMX-($C_4H_8O_8N_8$)-based propellant formulations.)

Little or no NO_2 results from the combustion of either Arcadene 311B or Chaparral under the conditions existing in the chamber used in this study. Low NO_2 generation has also been reported by other investigators.

The variations in removal of NO and CO may be due, at least in part, to the design of the excess air inlet system and the resulting uneven burning of the propellant and inadequate mixing of the gases in the chamber. These problems could be avoided by modifying the design of the chamber and by developing more effective means of providing air to the sample. For example, better mixing of the gases and a more even burn might be achieved by providing underflow and/or tangential air flow to the chamber. Investigation of these factors should be a major consideration in any future study.

Future work should be directed toward applying known or novel technology to changing the composition of the gases emitted to the atmosphere. A nickel oxide catalyst is reported[5] to accelerate the reaction of NO with CO:

$$2NO + 2CO \xrightarrow{NiO} 2CO_2 + N_2.$$

Nickel catalysts have been used successfully in a fluidized bed incinerator for the disposal of explosive wastes; NO, NO_2, and CO emissions were

reduced substantially[6]. Additions of catalysts to the filter bed should be evaluated as a means of reducing NO, NO_2, and CO emissions.

Similarly, while NO is a relatively difficult air pollutant to remove from a gas stream, NO_2 much more readily dissolves in water (ultimately forming nitric acid) and can be adsorbed on activated carbon though adsorption is poor for NO_2, but better than for CO and NO. Therefore, it would be advantageous to explore methods for rapidly converting NO to NO_2, such as by the addition of copper or other oxidation catalysts to the filter bed, or of determining whether catalyzed reduction (using NH_3) can be effectively applied.

SECTION 3

SYSTEM PREPARATION

EQUIPMENT

A schematic and a photograph of the combustion chamber are shown in Figures 1 and 2, respectively. The chamber was constructed of 3.2-mm (1/8-in)-thick steel. A 9-gauge (1.9-cm, 0.75-in.), slot-expanded sheet-metal grating located 30 cm (12 in.) from the top of the chamber provided the support for the sand and gravel filter. Hardware cloth was placed over this grating to prevent loss through the grating of smaller particles such as pea gravel and sand. The filter bed consisted of the following layers (bottom-to-top): 10 cm (4 in.) of road gravel, 5 cm (2 in.) of pea gravel, 2 cm (0.8 in.) of activated carbon, and 13 cm (5.2 in.) of sand. A 5-cm (2-in.)-thick layer of gravel was placed on the floor of the combustion chamber to provide a base for the propellant samples and to thermally insulate the bottom of the chamber and prevent warping; a drum lid provided the actual support for the propellant charge. A thermocouple placed immediately below the filter was used to determine the chamber temperature during each combustion test. One set of gas analyzer probes for NO, NO_2, and CO was placed below the filter to measure the gases resulting from the combustion process, and another set of probes was located above the filter to determine concentrations after passage through the filter. The probes were connected to the analyzers by 4.5-m (15-ft)-lengths of polypropylene tubing. A photograph of the experimental set-up is shown in Figure 3.

The following instruments and auxiliary equipment were used in the tests:

- Portable, direct-reading gas analyzers, Interscan Corporation, two each:
  - Nitric oxide (NO), 0 to 500 ppm.
  - Carbon monoxide (CO), 0 to 3000 ppm.
  - Nitrogen dioxide (NO_2), 0 to 500 ppm.
- Strip chart recorders:
  - 6-Channel, Brush-Gould Model No. 260 (to record output of gas analyzers).
  - Single channel, Sargent Model SR (to record output of thermocouple).
- Air flow meter, 0 to 18 m^3/min (0 to 600 cfm), Datamatrics Model 100VT.
- Battery charger, 12 VDC, plus nichrome wire for ignition.

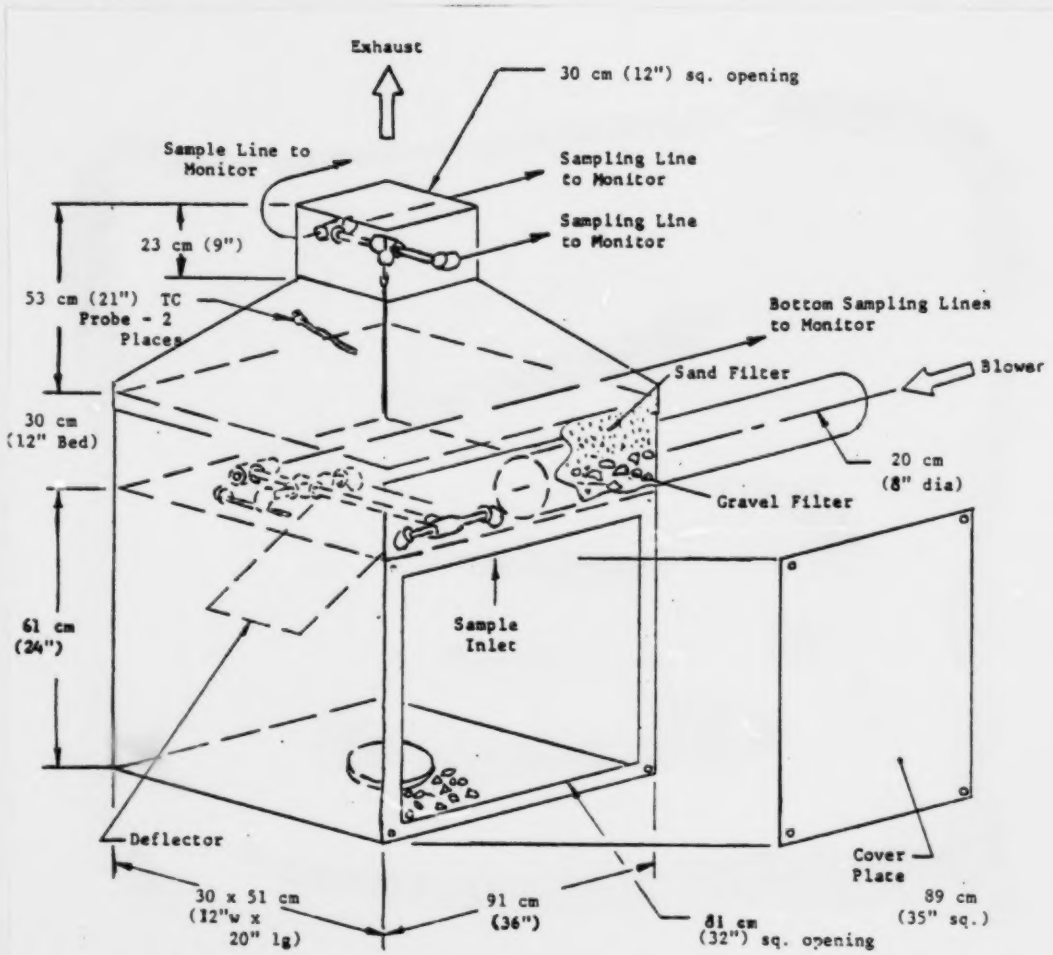
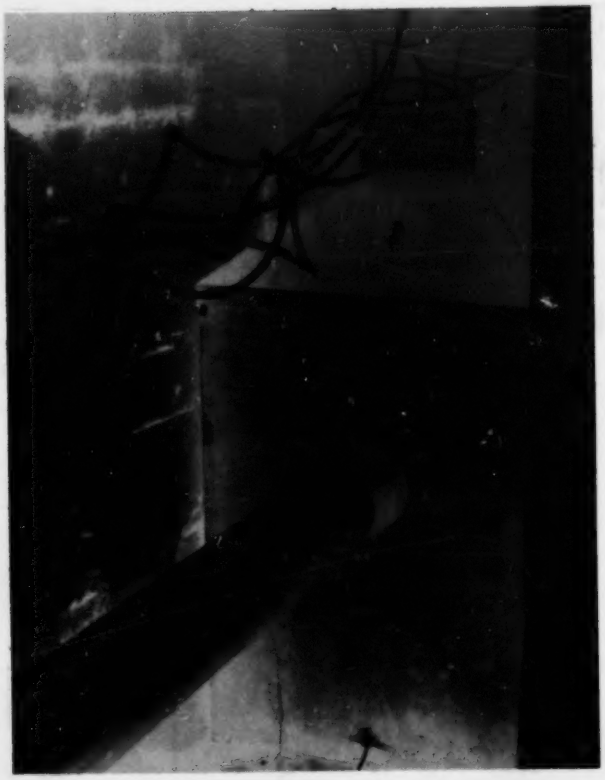
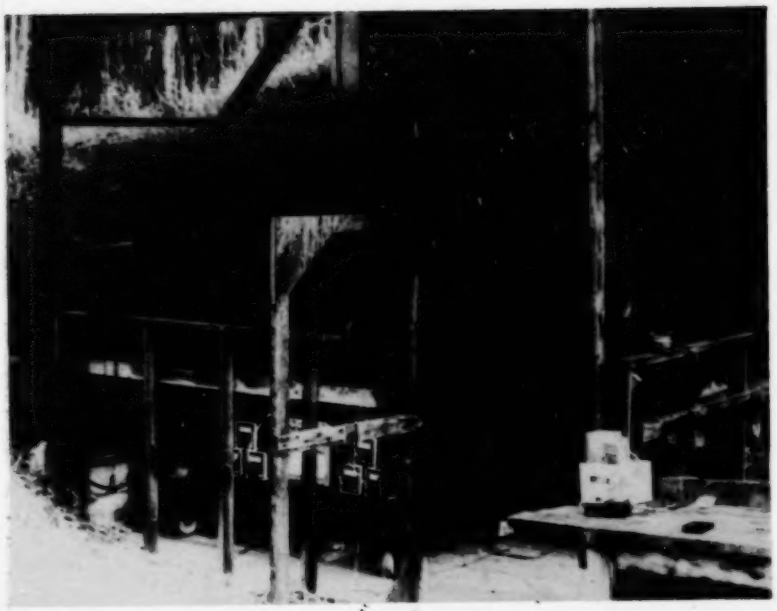


Figure 1. Schematic of combustion chamber.



1. Combustion chamber
2. Duct from blower to chamber
3. Polypropylene tubing from chamber to gas analyzers
4. Ignition wire

Figure 2. Combustion chamber.



1. Combustion chamber
2. Gas analyzers
3. 6-Channel strip chart recorder
4. Steel shield
5. Vent

Figure 3. Experimental set-up.

- o Thermocouples, type K, Chromel-Alumel, Omega Engineering.

- o Inlet filters for gas detectors
  gauze and activated charcoal, sealed canister type, Koby.
  coalescer/microfiber glass type, Balston.
  swinnex/Teflon element type, Millipore.

- * Tedlar gas sample bags, 1 liter.

- * Blower, 20-cm (8-in.) fan, 0.5 hp motor, 1.9-cm (0.75-in.)-Hg static pressure, Brundage Model SW-8-815.

- * Ducting, aluminum, 20 cm (8 in.) diameter (fan to incinerator).

EXPLOSIVES AND GASES

Two different propellants, Chaparral 6678 and Arcadene 311B (C-4), were used in the study to evaluate the effectiveness of the filter. General compositions of these two materials are given in Tables 1 and 2, respectively. In addition, black powder (74% potassium nitrate, 15.6% charcoal, and 10.4% sulfur) was used to study the air flow patterns in the combustion chamber.

The analyzers were calibrated as described in the next paragraph with EPA Protocol gases (1% certified) prepared by Scott Specialty Gases and having the following compositions:

CO in air, 350 ppm;
CO in air, 2000 ppm;
NO in H_2, 22 ppm; and
NO_2 in air, 250 ppm.

PROCEDURES

The gas analyzers were calibrated by attaching a gas bag filled with the appropriate Protocol gas to the gas inlet of the analyzer. Gas was allowed to pass through the sensor for approximately 1 min. For the calibration, the span control was adjusted so that the meter reading corresponded to the known gas concentration. Since the response of the instrument was--according to the manufacturer--linear with concentration, calibration of each type of analyzer at a single gas concentration was deemed sufficient.

The combustion chamber was prepared for air flow optimization tests by replacing the steel cover plate with one constructed of plywood and having a Plexiglas™ window. The filter bed was prepared as it would be for an actual burn. Air flow was provided by the blower, and smoke--used in observing the air flow patterns--was generated by igniting a small quantity (approximately 20 g) of black powder in the chamber. A temporary plywood deflector was placed in a different position within the chamber for each run. When thorough mixing of the smoke within the chamber appeared to have been achieved, the deflector position was noted so that a permanent steel baffle could be attached at that position.

TABLE 1. APPROXIMATE COMPOSITION OF CHAPARRAL 6678 PROPELLANT

Component	Weight % of Total
HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine)*	60
Nitroplasticizers	27
Polyester resins	6
Nitrocellulose	1.5
Caprolactone polyol	1.5
Other (minor constituents)	4.0
2-Nitrodiphenylamine	
4-Nitrodiphenylamine	
N-Methyl-p-nitroaniline	
Diisocyanate	
Carbon black	
Zirconium carbide	
Tin oxide	
Lead sesquioxide	
Triphenylbismuth	

* Cyclotetramethylenetetranitramine ($C_4H_8O_8N_8$)

TABLE 2. ARCADENE 311B (C-4) COMPOSITION

Component	Weight % of Total
HMX	84.80
Carbon black	0.05
Curative and binder	15.15

SECTION 4

EXPERIMENTAL PROCEDURES

The chamber was prepared for the ignition of the propellants by assuring that the bed contained sufficient moisture to be "damp". The bed was kept moist for two reasons; first, to maintain structural integrity and, second, so that NO and NO_2 (if present) could be absorbed and, possibly, converted to nitrogen-containing acids. The reactions of NO and NO_2 with oxygen and water to form nitric and nitrous acids are complex and will not be discussed. (Activated carbon was included in the bed because it is known to adsorb NO_2; NO is not significantly adsorbed, nor is CO.)

The cast propellant blocks had the consistency of soft rubber and were easily sliced with a knife. The blocks were cut into slabs measuring approximately 15 x 10 x 2.5 cm (6 x 5 x 1 in.) for each test. Each slab was weighed and then prepared for ignition by placing a 20-cm (8-in.)-length of nichrome wire into a cut made near one end of the slab. The ends of the nichrome wire were attached to leads of the battery charger by means of alligator clips. (Hot nichrome wire can ignite the propellants used.) A sketch of a slab of Chaparral (approximately 500 g) prepared in this manner is shown in Figure 4. In preparation for the test, the sample was placed in the chamber, and the metal cover plate was bolted over the chamber sidewall opening (Figure 1).

Before the actual ignition of the propellant samples, the gas analyzers were wired to the six-channel strip chart recorder and activated. The analyzers were zeroed, and chart speed and analyzer output sensitivities were selected. The single-channel recorder for chamber temperatures was plugged in and turned on. The blower providing air to the chamber was also turned on.

When the above procedures were complete, the propellant sample was ignited by switching the battery charger on and allowing current to flow through the nichrome wire embedded in the propellent sample until the generation of smoke--or a rise in temperature--indicated that ignition had taken place. The battery charger was then switched off. Exhaust rates were measured during the burning of the propellant by holding the probe of a portable, hand-held air flow monitor over the exhaust stack of the chamber. Temperature and gas concentration data were collected until NO, NO_2, and CO concentrations above and below the filter returned to zero. The time until gas evolution ceased was recorded in some tests.

Gas concentration data were obtained in terms of peak concentrations and, in certain cases, also as time-averaged concentrations. According to the manufacturer, the voltage output of the analyzer is proportional to gas

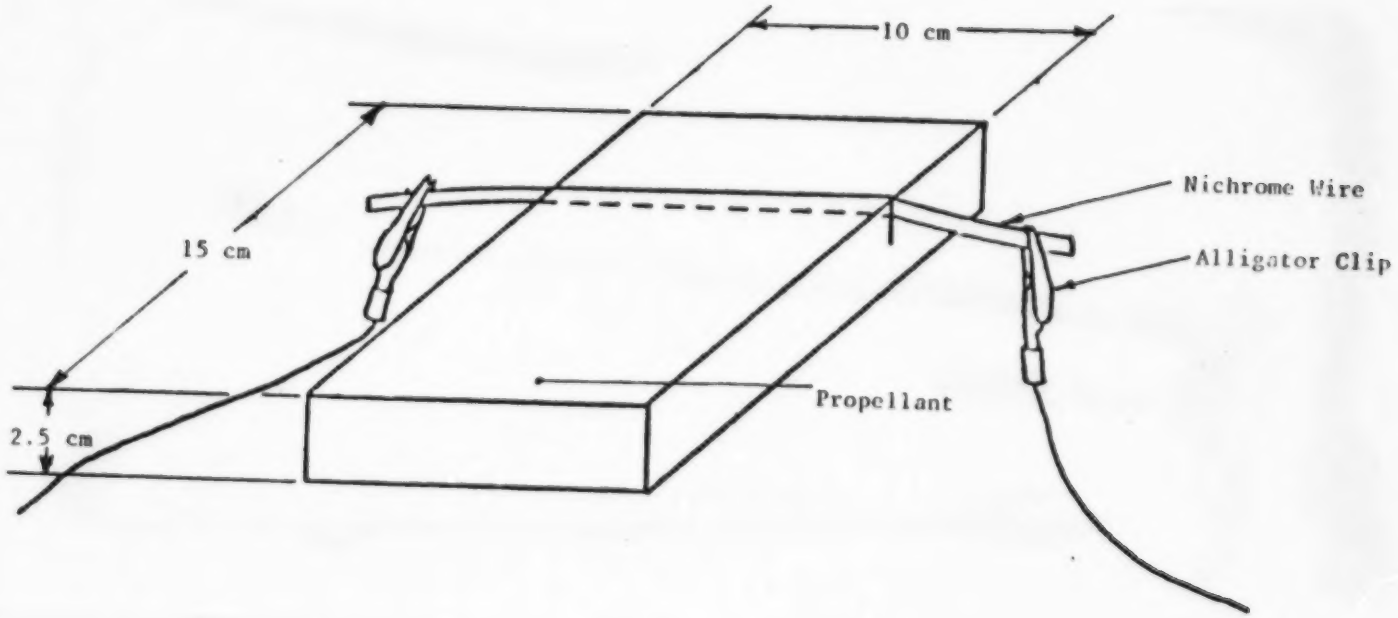


Figure 4. Slab of Chaparral propellant prepared for ignition.

concentration. Time-averaged concentrations, i.e., the average concentrations over the time during which gas was evolved, were determined by measuring the area under a plot of the gas concentration against time on the recorder chart with a calibrated planimeter. The measured area was then divided by the total time during which gas was emitted to yield the average concentration.

PRELIMINARY TEST BURNS

A series of preliminary test burns was carried out to determine the minimum sample size needed to produce measurable concentrations of CO and NO_x and to select the appropriate analyzer output sensitivities. For example, an initial test burn of 100 g of Chaparral produced negligible NO_x and CO emissions; therefore, sample size was increased. Chaparral samples in the range of 200 to 500 g were found to produce adequate gas volumes. Smaller samples of C-4 (approximately 100 to 200 g) were found to be adequate, because of the higher content of HMX explosive in this propellant.

The preliminary test burn data were also used to optimize burn conditions. The goals of this optimization were to provide sufficient combustion air and yet to maximize the residence time of the gases in the filter bed. To meet these requirements, the blower that provided air to the chamber was modified to allow the air flow to be decreased. This was accomplished by systematically restricting the air intake to the blower. At each change (reduction) in air flow, the rate of air flow was measured at the inlet to the combustion chamber. This procedure was repeated until the levels of CO within the chamber (below the filter bed) began to increase, indicating insufficient excess air to ensure combustion of the CO to CO_2. This air flow (2.4 m^3/min (85 ft^3/min)) rate was then used for all the burns of record.

SECTION 5

RESULTS AND DISCUSSION

Including the preliminary burns used to establish the correct minimum air flow rate (but excluding the black powder burns), a total of 42 test burns were carried out during the course of this study: 25 with Chaparral and 17 with C-4 (Arcadene). Of this total, the last 14 burns used the 2.4 m^3/min air flow rate. Table 3 is a summary of the results of all 42 tests. As noted earlier, gas composition varied widely, even with similar sample sizes and air flows. For example, test runs 28, 32, 33, and 34 all used approximately 55 g of Chaparral and 2.4 m^3/min air flow and generated a chamber temperature of about 400°C. Nevertheless, peak NO concentrations ranged from 300 to 600 ppm before the filter and 300 to 400 ppm after the filter. Carbon monoxide was present only is test 28. In most of the runs, little or no NO_2 was found. There was no apparent relationship betwen NO_2 gas concentration and sample size or air flow.

In spite of the high variability, inspection of the data and detailed comparison of the gas compositions before and after filtration indicated that the passage of the gas through the filter bed does remove varying amounts of the nitric oxide and carbon monoxide. Nitric oxide was the predominant product: wide fluctuations occurred in carbon monoxide peak concentrations. The results of test burns 28 through 42 are also shown in Tables 4 and 5. In these two tables, all gas concentration data are time-averaged values. Nitric oxide remains the predominant gaseous product of the three being analyzed. It is apparent from these data that the large fluctuations noted in the peak values of Table 3 also exist in the time-averaged measurements. For example, in the burning of Chaparral, time-averaged concentrations of NO (before the filter) ranged from 94 to 295 ppm and CO concentrations ranged from 0 to 434 ppm. The decomposition of C-4 generated NO concentrations (before the filter) ranging from 182 to 676 ppm and CO concentrations of 0 to 475 ppm. These fluctuations may reflect, at least in part, insufficient mixing of the gases within the chamber or uneven burning of the propellant. Insufficient gas mixing or uneven burning may be responsible for localized variations in the gas concentrations within the chamber, which are detected by the gas analyzer probes.

The primary objectives of this study were (1) to measure the NO, NO_2 and CO levels in excess air combustion and (2) to determine the effectiveness of the sand and gravel filter. In view of the wide fluctuations in gaseous emissions, it was difficult to quantify the concentrations or the filter effectiveness. Nevertheless, percent-reduction data in Tables 4 and 5, based on time-averaged concentrations, do confirm that significant reductions were produced by the filter. For Chaparral burns, the percent reduction in NO across the filter bed ranged from 10 to 57%; for CO the range was 33 to 91%.

TABLE 3. COMBUSTION OF CHAPARRAL AND ARCADENE 311B (C-4)

Burn #	Propellant	Propellant Weight (g)	Air Flow Rate (m3/min)	Chamber Temperature (°C)	Maximum Gas Concentrations (ppm) Bottom NO	Bottom CO	Bottom NO_2	Top NO	Top CO	Top NO_2
1	Chaparral	450	6.4	-	-	>3000	-	-	>3000	-
2	Chaparral	340	6.4	-	250	-	-	205	0	0
3	Chaparral	450	6.4	-	250	175	5	250	0	10
4	Chaparral	450	6.4	-	250	>3000	5	250	>3000	10
5	Chaparral	225	6.4	-	250	0	10	200	0	5
6	C-4	225	6.4	-	250	0	30	250	0	10
7	C-4	225	6.4	-	250	0	125	250	0	0
8	C-4	225	6.4	-	-	-	-	-	-	-
9	C-4	225	6.4	180	360	0	50	200	0	25
10	Chaparral	630	6.4	299	370	>3000	15	190	0	0
11	Chaparral	180	6.4	136	125	0	-	80	0	0
12	C-4	180	6.4	147	375	0	50	210	1200	0
13	C-4	180	6.4	166	320	0	40	170	0	0
14	C-4	180	6.4	173	360	0	10	130	0	0
15	C-4	180	6.4	155	200	0	10	130	0	0
16	C-4	180	6.4	130	200	0	15	120	0	0
17	Chaparral	545	6.4	311	260	0	15	120	0	0
18	Chaparral	545	6.4	342	140	0	10	150	0	0
19	Chaparral	480	3.9	370	>500	0	5	180	0	0
20	Chaparral	446	2.9	366	>500	0	0	200	0	0
21	Chaparral	474	1.0	326	500	0	0	130	0	0
22	Chaparral	211	1.0	282	>500	0	0	110	0	0
23	Chaparral	498	1.0	355	210	>3000	0	230	>3000	0
24	Chaparral	493	1.0	420	>500	600	0	175	900	2
25	Chaparral	248	1.0	278	>500	450	0	175	300	0
26	Chaparral	435	1.0	370	1250	2100	0	175	750	0
27	Chaparral	476	1.5	318	950	975	0	225	300	0
28	Chaparral	522	2.4	370	525	1050	5	275	225	0
29	C-4	162	2.4	194	525	150	5	250	75	0
30	C-4	65	2.4	92	150	-	-	125	-	-
31	C-4	70	2.4	172	1300	0	0	600	600	55
32	Chaparral	503	2.4	376	600	0	0	400	0	10
33	Chaparral	493	2.4	394	350	0	10	300	0	0
34	Chaparral	528	2.4	416	300	0	0	300	0	0
35	C-4	129	2.4	-	700	600	0	250	150	20
36	C-4	114	2.4	131	450	0	0	100	0	0
37	C-4	114	2.4	139	400	0	0	100	0	0
38	C-4	103	2.4	153	1100	30	2	250	0	5
39	C-4	94	2.4	-	1150	450	20	325	270	15
40	Chaparral	200	2.4	190	200	9	0	100	0	0
41	Chaparral	500	2.4	380	200	30	0	150	15	0
42	Chaparral	500	2.4	-	200	45	0	150	15	0

TABLE 4. COMBUSTION OF CHAPARRAL 6678

Burn Number	Weight (g)	Chamber Temp. (°C)	Gas Concentrations* Bottom (ppm)			Top (ppm)			% Reduction	
			NO	CO	NO_2	NO	CO	NO_2	NO	CO
40	200	190	110	0	0	56	0	0	49	-
33	493	394	171	0	0	153	0	0	10	-
41	500	190	94	23	0	71	3	0	24	81
42	500	-	117	27	0	74	18	0	37	33
32	503	376	295	0	0	202	0	0	32	-
28	522	-	148	434	0	63	40	0	57	91
34	528	416	249	0	0	171	0	0	31	-

*Time-averaged concentrations

TABLE 5. COMBUSTION OF ARCADENE 311B (C-4)

Burn Number	Weight (g)	Chamber Temp. (°C)	Gas Concentrations* Bottom (ppm)			Top (ppm)			% Reduction	
			NO	CO	NO_2	NO	CO	NO_2	NO	CO
31	70	172	676	475	0	304	88	7	55	81
39	84	-	535	212	7	204	132	8	62	38
38	103	153	372	0	0	105	0	2	67	-
36	114	131	205	0	0	69	0	0	66	-
37	114	139	182	0	0	78	0	0	57	-
29	162	194	185	114	0	138	40	0	25	65

*Time-averaged concentrations

The percent reduction in NO generated by the excess air destruction of C-4 ranged between 25 and 67%, and the CO reduction ranged from 38 to 81%. Insufficient mixing of gases and uneven burning, as discussed earlier, may be responsible for these variations. Nevertheless, it is significant that reductions in both NO and CO did occur consistently.

The absence of significant concentrations of NO_2 was expected. Other studies[3] under different conditions have shown that the primary isothermal degradation products of HMX are N_2O, N_2, NO, CO, CO_2, and HCN. For example, the yield of gaseous products from the isothermal decomposition of HMX [7] at selected temperatures is shown in Table 6. It should be noted that these values are the result of isothermal degradation of HMX, not an incinerative process such as used in the present study; therefore, the results should only be used as indicative of the relative amounts of off-gases. These values also do confirm the observed absence of NO_2 in the current study.

TABLE 6. YIELD OF SELECTED GASEOUS PRODUCTS FROM THE ISOTHERMAL DEGRADATION OF HMX

Temp. (°C)	N_2O	N_2	NO	CO	CO_2	HCN
	(moles gas produced/mole HMX charged)					
226	2.52	0.47	0.42	0.40	0.56	0.02
250	2.58	0.46	0.50	0.47	0.41	0.04
258	2.57	0.47	0.55	0.47	0.54	0.07

Exhaust rates were also determined for two samples at the established blower rate. The burning of a 522 g sample of Chaparral gave a peak exhaust rate of 1.4 m^3/min while 162 g of C-4 produced a peak exhaust rate of 1.8 m^3/min. These values again reflect the higher HMX content of the C-4 propellant.

Over the period of 1971 to 1976, Mason and Hanger-Silas Mason Co., Inc., investigated various methods for the disposal of high explosives. As part of that study, PBX 9404, an HMX-based, plastic-bonded explosive ("PBX"), with the composition shown in Table 7, was thermally decomposed in a closed-pit chamber (bunker) designed to accommodate approximately 450 kg (1000 lb) of explosive. As part of that study, a sand filter placed above the chamber was evaluated, primarily for the control of particulate emissions. Because of the similarities between the Mason and Hanger work and the present study, a comparison between the results of the two is of interest. Data selected and adapted from the earlier study [4] are presented in Table 8. Maximum values for NO_x emissions were of the same order of magnitude as those found in the current study, but the levels of CO reported by Mason and Hanger were much higher than those found in the

Table 7. COMPOSITION OF PBX 9404*

Component	% of Total
HMX	94 ± 0.5
Nitrocellulose	3
CEF	3
Diphenylamine	0.1 ± 0.01

* Reference 8.

Hanger were much higher than those found in the current study, probably because the large volume of excess air introduced in the current study converted more CO to CO_2. Although percent reduction values after passage through the filter are not given in the Mason and Hanger report, the authors did note that slight decreases in NO_x and CO emissions were measured as the gases passed through the filter. The authors also found that, at most, 10% of the NO_x was in the form of NO_2, and that the major component of the NO_x was NO. Temperatures of the chamber, also noted in Table 8, were obtained on an I-beam support above the pit; they are of the same order of magnitude as those measured in the current study.

TABLE 8. SELECTED DATA FROM HIGH EXPLOSIVE INCINERATION*

Burn No.	Amount of HE (kg)	Burn Time (min)	Temp. (°C)**	Peak Gas Concentrations NO_x (ppm)	CO (ppm)
40	463	1.08	370	275	60,000
41	457	1.17	370	277	44,000
45	463	1.19	370	500	18,000
47	463	1.19	320	502	5,000
48	457	1.28	350	375	11,000
52	463	1.11	340	476	3,900

* Reference 4.
** Temperature of I-beam located in incinerator.

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